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Optical properties of *para*-hexaphenyl polycrystalline films

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Abstract

We investigate the optical properties and intermolecular coupling of *para*-hexaphenyl polycrystalline films by site-selective spectroscopy, time-resolved photoluminescence and photoinduced absorption measurements. Our results point to (i) a short-range orientational and energetic disorder and (ii) the molecular character of the light emission, with no evidence of intermolecular excited states. © 1998 Elsevier Science B.V.

1. Introduction

Para-hexaphenyl (PHP) is successfully used in highly efficient electroluminescent devices emitting blue light [1–3]. Moreover, bright red–green–blue emitting devices using an all organic color conversion technique based on organic dyes pumped with PHP diodes have been recently realized [4,5]. Homogeneous PHP thin films can be prepared by evaporation on different substrates and, depending on the evaporation conditions, different degrees of crystallinity and molecular orientation can easily be obtained [6]. A complete optical investigation of *para*-hexaphenyl is therefore particularly needed for their exploitation in light emitting devices and lasers.

Intermolecular excited-state interactions can take place in organic materials, leading to different excited species, e.g. Frenkel excitons, dimers, etc. In polycrystalline films of π-conjugate oligomers, intermolecular interactions can favour the formation of nonradiative excitons (H-aggregates), as suggested for oligothiophene films [7–10]. Since photoluminescence (PL) measurements allow to reach direct information on the radiative and nonradiative decay pathways, in this paper we use steady-state and picosecond time-resolved PL measurements in PHP polycrystalline films to study the effects of intermolecular interactions and the photoexcitation formation and decay. Combined time-resolved photoinduced absorption (PA) measurements allow us to identify the emissive species.

2. Experimental

Highly purified PHP was evaporated in high vacuum ($< 10^{-6}$ mbar) onto sapphire kept at room temperature, obtaining PHP polycrystalline layers a few 1000-Å-thick. X-ray studies indicate that crystallites with arbitrary orientation are grown.

Femtosecond pump and probe experiments were performed using a $TiAlO_3$ laser system with chirped

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pulse amplification, delivering pulses of 150 fs duration. The details of the set-up are described elsewhere [11]. The samples, kept at room temperature, were pumped by pulses at 3.2 eV with energy ranging from 5 to 130 nJ and a 1 kHz repetition rate.

Spontaneous emission was excited by the fourth harmonic of a pulse-compressed Nd:YAG laser delivering 4-ps-long pulses, or by the second harmonic of a synchronously pumped dye-laser delivering 0.5-ps-long pulses. Spectral resolution was obtained by means of spectral filters or through a monochromator. Temporal dispersion of the signal was achieved through a Hamamatsu optical sampling oscilloscope, which combines a high time-resolution (20 ps) with a high dynamical range.

The steady-state PL spectra were recorded upon excitation with the second harmonic of the dye-laser. Excitation energies ranging from 3.01 to 3.3 eV were used.

3. Results and discussion

In Fig. 1 we report the absorption spectrum and the steady-state photoluminescence at 300 and 10 K. The absorption curves show a large band centred near 3.8 eV. The bandwidth is about 1 eV and no vibronic fine structure is resolvable at room temperature. While the absorption spectrum is poorly structured even at low temperature, the PL spectra consist

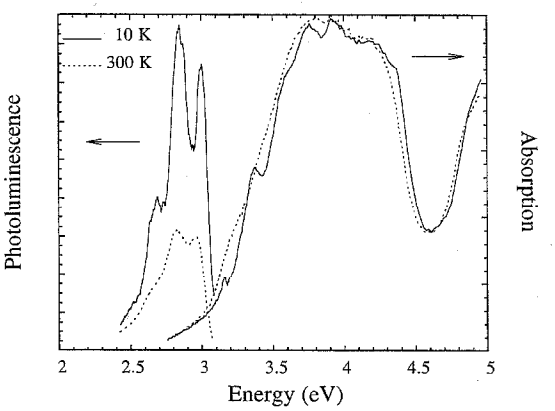

Fig. 1. Room (dashed lines) and low-temperature (continuous lines) absorption and photoluminescence spectra of *para*-hexaphenyl film.

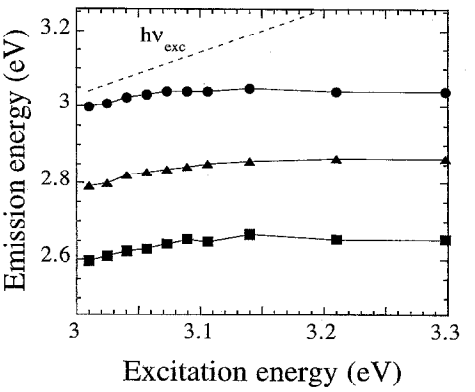

Fig. 2. Peak energies of the 0–0, 1–0 and 2–0 vibronic emissions versus excitation energy $h\nu_{exc}$. $T = 10$ K.

of a main band followed by a vibronic progression which becomes much more evident when temperature is lowered. The absorption maximum and the highest-energy luminescence peak are separated by about 0.8 eV.

In conjugated polymers, most of the inhomogeneous broadening of the optical absorption comes from the conjugation length distribution [12,13]. On the other hand, molecular crystals such as PHP films possess well defined oligomer lengths. The large broadening of the absorption spectrum may be mainly ascribed to conformational disorder, i.e. variety of oligomer geometrical arrangements due to the torsional degree of freedom of adjacent rings. The deviation from the mirror image rule between absorption and luminescence spectra at 10 K suggests that the conformational disorder persists even at low temperature, pointing to the minor role of dynamical effects like conformational mobility (ring libration) and supporting its static nature. Moreover, a further contribution to the PHP broad absorption band could come from short-axis polarised transitions [14,15], which are expected at energies higher than the ones polarised along the long axis.

The PL quantum yield of our PHP films is 0.30 at room temperature [16], much higher than for oligothiophene and oligophenylenevinylene films (10^{-3}–10^{-2} and < 0.1, respectively [8,9,17]). This indicates that the H-aggregate exciton model, successfully invoked for oligothiophene and oligophenylenevinylene films to account for the absorption lineshape and the low luminescence quan-

tum yield [7–10], does not hold in PHP. In order to investigate the intermolecular organization, we have performed steady-state polarized luminescence measurements by detecting the PL intensity emitted with polarization parallel to the incoming laser, I_{par}, and with polarization perpendicular to the laser, I_{perp}. We have found that the cw-photoluminescence depolarization ratio $\rho = I_{par}/I_{perp}$ is 1.3 for all the emission energies (for a film constituted by randomly oriented domains, the upper limit is 3). Since polarization-memory loss in condensed systems is due to excited state migration to differently oriented molecules, this low luminescence anisotropy implies that absorbing and emitting molecules are differently aligned.

The influence of disorder on the emission and relaxation processes has been more deeply explored by site-selective photoluminescence spectroscopy. Measurements have been performed by detecting the photoluminescence spectra at 10 K with the excitation energy ranging from 3.3 eV down to the tail of the absorption band. Our results are summarized in Fig. 2, which reports the spectral position of the three PL main peaks as a function of the excitation energy. We observe that for excitation energies be-

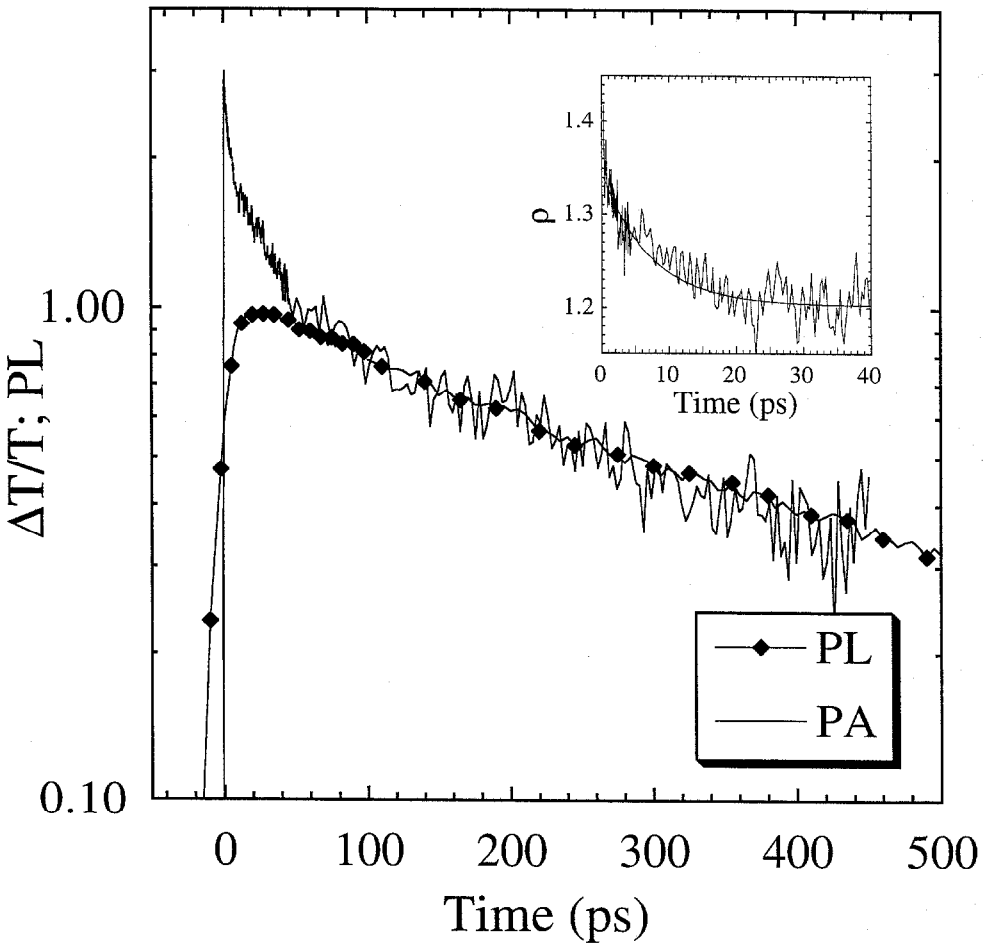

Fig. 3. Room temperature transient dynamics of the spectrally integrated PL compared with PA detected at 1.65 eV (the excitation energy is 3.3 and 3.2 eV, respectively). Inset: dynamics of the photoinduced absorption anisotropy $\rho = \Delta T_{par}/\Delta T_{perp}$. The continuous line is the best fit to the experimental data using the expression $ae^{-t/\tau} + c$.

low approximately 3.1 eV the emission is quasi-resonant with the laser energy, while for excitation energies greater than 3.1 eV the emission spectrum is independent of excitation.

Our findings are similar to those reported for conjugated polymer films [12,18,19], and can be explained assuming that photoexcitations undergo spectral diffusion within an inhomogeneously broadened density of energy states introduced by disorder. If excited above the 'localization threshold' E_{loc}, they release part of their energy by relaxation first to the lowest-energy vibrational level and then toward lower energy sites. If excited below E_{loc}, spectral diffusion is considerably inhibited, because adjacent sites with lower energies are no more available within the lifetime of the excited species. Our data indicate that intramolecular geometrical relaxation of the emitting cromophores causes a small shift (< 40 meV) between excitation and emission in PHP.

Fig. 3 compares transient photoinduced absorption and spectrally integrated photoluminescence at room temperature. The PL decay shown has lifetime $\tau_{PL} = 400$ ps (by lowering the temperature it tends to 1 ns), whereas a biexponential decay with time constants of 29 and 400 ps describes the PA detected at 1.65 eV. PA is faster than PL below 40 ps, while from 40 to 400 ps PL and PA dynamics coincide. The initial faster decay of PA with respect to PL, as measured by the fs system, is accounted for by bimolecular singlet annihilation caused by the high excitation intensity, which is 3–4 order of magnitude greater than in PL measurements.

The results reported in Fig. 3 support the hypothesis that at early times following the photoexcitation the same species, with intrachain character, are involved in emission and absorption. Although photoabsorbing interchain species occur in PHP, their photogeneration is not a very likely mechanism, since we observe that PA and PL have the same dynamics and PL is definitely related to single molecule emission.

In time-resolved polarized photoluminescence, the depolarization ratio reaches 1.3 within the time resolution of our apparatus (20 ps) and does not change for longer times (up to 5 ns). Transient PA measurements at 1.65 eV with pump and probe parallel and pump and probe perpendicular are summarized in the inset of Fig. 3 by showing the decay of the photoinduced absorption depolarization ratio ρ. Theoretically, the depolarization ratio in a randomly oriented ensemble of emitters should be 3 initially. On the other hand, we find 1.36 within the temporal resolution (200 fs). We detect a slower decay (7 ps), followed by a plateau where $\rho = 1.2$, i.e. very close to the value found in PL experiments. Therefore, the dichroic measurements indicate that the correlation length of orientational disorder is short.

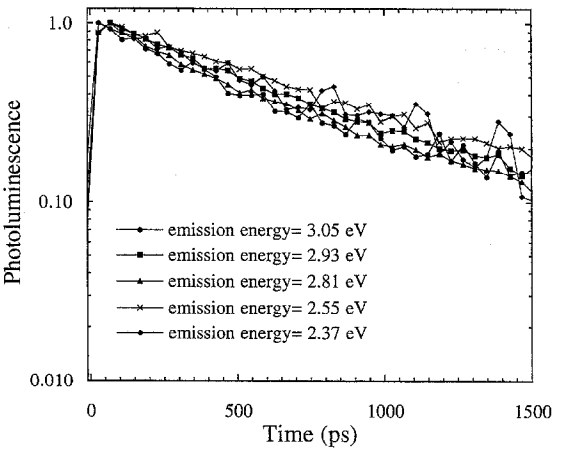

Fig. 4. Photoluminescence decays at different emission energies in PHP. Spectra are normalized to the maximum intensity. $T = 10$ K and $h\nu_{exc} = 3.3$ eV.

We have investigated the PL dynamics both at 10 and 300 K as a function of the detection energy. Scanning the emission energy from 2.4 to 3 eV results in similar PL traces, as shown in Fig. 4 for $T = 10$ K. τ_{PL} does not change appreciably for all the emission energies. Moreover, energy migration of the photoexcitations should lead to a transient spectral shift of the emission which is not evident in the time domain of our PL data. These findings indicate that (i) the photoluminescence peaks are vibronic components of the same transition and (ii) spectral diffusion is extremely slow at times longer than 30 ps.

4. Conclusions

Our investigations prove that highly luminescent *para*-hexaphenyl polycrystalline films are ensemble of weakly interacting molecules and display mainly

intramolecular optical properties. Moreover, the same photoexcited species are responsible for both absorption and emission processes. The features typical of the exciton coupling have not been observed. In particular, the lowest-energy emission, which is completely forbidden in H-aggregates, is permitted, giving rise to the high photoluminescence quantum yield 0.3 of PHP in the solid-state.

Site-selective photoluminescence measurements indicate that the photoexcitations undergo spectral diffusion prior to recombination. For times longer than 20–30 ps, time-resolved photoluminescence data do not present nor spectral shift of the emission nor emission-dependent lifetimes, so that spectral diffusion is expected to occur for earlier times.

Dichroic PA and PL measurements show that polarization memory is almost completely lost within the first 10 ps after photoexcitation. This implies that the orientational disorder in PHP has a short correlation length, suggesting the existence of small quasi-crystalline domains with different orientations.

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